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SUMMARY

Sediments act as sources and sinks for many compounds and elements. Trace metals and organic contaminants have a high particle affinity and can be absorbed or released by sediments; a large fraction of the elements that take part in the biological cycles (C, N, P) are mineralized in the sediment, and carbon dioxide, nitrate, and phosphate are released to the water column. Therefore, the study of fluxes between sediment and water column is important for the understanding of contaminant concentrations and eutrification levels. Solute fluxes can be studied in the laboratory by confining a sediment sample and a volume of overlying water in a microcosm. Since the hydrodynamical conditions at the sediment water interface determine the solute exchange flux, the hydrodynamical calibration of microcosms is important. In this thesis a microcosm with calibrated hydrodynamics is evaluated. Measurements of oxygen fluxes to the sediment, and organic contaminant fluxes from the sediment are discussed.

In Chapter 1, the hydrodynamical characteristics of the benthic boundary layer and its relevance to exchange rates of solutes between sediment and water is discussed. The hydrodynamical calibration of a microcosm is evaluated. The bottom shear stress in this microcosm can be varied at will for environmentally relevant settings, and is homogeneous except for a small area at the centre of the microcosm. For the transport between the sediment water interface and the water column, vertical currents in the microcosm are expected to overrule transport of solutes by diffusion. However, no indication was found for the existence of vertical currents in the pore water.

Chapter 2 deals with the sensitivity of some oxygen microelectrodes to water flow velocities. The current-output by oxygen microelectrodes in water decreases substantially at low flow velocities because of the increased importance of the mass transfer resistance that is posed by the boundary layer surrounding the probe. The magnitude of this velocity effect increases with increasing sensitivity of the probe. Depending on the probe, 10 to 50% reductions in current output were observed. Before using microelectrodes to measure oxygen in pore water, they must be tested for the magnitude of the velocity effect and, if necessary,

calibrated in zero-flow water. Caution is advised in interpreting data obtained with oxygen microelectrodes in the low velocity region near solid-fluid interfaces unless both the velocity gradient in this region and the velocity effect of the electrode are known.

The response of oxygen distributions to changes in the flow velocity of the overlying water is discussed in chapter 3 for a sandy sediment. The oxygen penetration depth in the sediment increased more than threefold when the flow velocity was increased from 0 to 15 cm s^{-1}, corresponding to a friction velocity range of 0 to 1 cm s^{-1}. The oxygen flux to the sediment also increased. The oxygen profiles responded within seconds to minutes to a change in the flow velocity. The steady state distributions of oxygen can be described by a one dimensional transport-reaction model that assumes zero-order reaction kinetics. Transient states can be modeled by assuming, in addition, that the diffusion in the pore water responds instantaneously to changes in the water flow velocity. Effective diffusion coefficients increased with increasing flow rates from $3 \cdot 10^{-9}$ to $2 \cdot 10^{-7}$ m^2 s^{-1}, compared to a molecular diffusion coefficient in the pore water of $1 \cdot 10^{-9}$ m^2 s^{-1}.

The experiments were extended to include a muddy sediment (Chapter 4). The effect of changing the water flow velocities on the distribution of oxygen in the pore water and the flux of oxygen across the sediment water interface was studied. Increasing the friction velocity increased both the oxygen flux and the penetration depth of oxygen in the sediment. Increased diffusion in the pore water is an important mechanism responsible for this effect. Changes in the boundary layer resistance, and oxygen consumption in the water column by resuspended particles, were less important. The oxygen distribution in the pore water and the transition from one steady state to another, following a change in either the friction velocity or the oxygen concentration in the water column, can be described by a diffusion/zero order reaction model. The model is improved when it is assumed that the diffusion coefficient decreases exponentially with depth. Effective diffusion coefficients are close to the molecular value of $1 \cdot 10^{-9}$ m^2 s^{-1}. However, some measurements indicated that near the sediment water interface effective diffusion coefficients are a factor of 4-60 higher, depending on the water flow rate.

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In contrast to the two previous chapters, Chapter 5 deals with solutes that are released by the sediment. Fluxes of individual chlorinated hydrocarbons were measured by circulating the overlying water in the microcosm continuously through a liquid-liquid extractor, and sampling the extracts at regular times. In order to obtain reliable flux measurements, contaminant concentrations in the water column must be much smaller than concentrations in the pore water. A set of criteria was developed to accomplish this. The release rates, can be described by a diffusion model with an effective diffusion coefficient of $3 \cdot 10^{-8}$ m^2 s^{-1}, which is approximately two orders of magnitude higher than the molecular diffusion coefficient. The relative importance of diffusion, sediment reworking by benthic organisms, and particle resuspension is evaluated. With ongoing sedimentation of uncontaminated suspended matter, contaminated sediments are ultimately buried. It is estimated that sediments can act as secondary sources of organic contaminants for several centuries, before release rates are outweighed by sedimentation rates.

The results for oxygen fluxes show that flow induced diffusion is an important transport mechanism for solutes. For sandy sediments increased diffusion is apparent over a distance of 5-10 mm down into the sediment. For muddy sediments flow induced diffusion is limited to a narrow region near the sediment water interface. Effective diffusion coefficients for organic contaminants agree well with values obtained from the oxygen flux measurements. The significance of these results is that both for sands and for muds there is no region close to the sediment water interface where transport by molecular diffusion dominates over transport by convection, except for very low flow rates. This also means that the hydrodynamical calibration of microcosms is a prerequisite for reliable flux measurements.